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(54) PRODUCTION OF BROMINATED POLYSTYRENE FROM RECOVERED POLYSTYRENE FOAM

(57)Abstract:

PURPOSE: To effectively utilize a recovered waste polystyrene foam by pulverizing or pelletizing it or reducing its volume, dissolving it in a halogenated hydrocarbon solvent to remove impurities, and brominating the soln. to produce a brominated polystyrene.

CONSTITUTION: A recovered polystyrene foam, pref. contg. 80wt.% or higher styrene units and from which foreign matters have been removed, is granulated, then pulverized or pelletized by melt extrusion with an extruder followed by cutting, and dissolved in a halogenated hydrocarbon solvent (e.g. ethylene dichloride). From the resulting soln. are removed solvent-insol. matters by filtration, etc., and pref. by further filtration after adsorbing the insol. matters with an adsorbent, e.g. diatom earth. Polystyrene dissolved in the solvent is brominated with bromine, etc., at -20 to 100°C using a catalyst, e.g. anhydrous aluminum chloride. After the completion of bromination, the reaction soln. is washed with water, neutralized, and distilled to remove the solvent, thus giving a brominated polystyrene.

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CLAIMS

[Claim(s)]

[Claim 1] How to dissolve the collected form polystyrene in a halogenated hydrocarbon solvent grinding or after reducing the volume or pelletizing, to remove insoluble matter, to brominate this solution subsequently, and to manufacture bromination polystyrene.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the approach of manufacturing bromination polystyrene useful as a flame retarder of inflammable resin from recovery form polystyrene.

[0002]

[Description of the Prior Art] Form polystyrene is excellent in adiathermic, its degree of hardness is high, and its water absorption is small, it is excellent in the water resisting property, and excellent in impact absorptivity. Moreover, it is white and coloring is also easy, and since [with a beautiful appearance] it is comparatively cheap, it is broadly used for the rose-like shock absorbing material for a foaming board and package shock absorbing material used for the foaming sheet used for food containers, such as the bead foaming article and food-grade tray which are used for a home wrapping material or the fish box for fishery, and instant noodles, etc., the building-materials application which makes a heat insulator a subject.

[0003] However, processing of a plastic waste and playback-ization serve as an important problem of an environmental problem like [form polystyrene] other plastics. And since the volume is large as dust, form polystyrene is the target of waste treatment and is in the present condition which the related industry is united at last and began to start recycle activities.

[0004]

[Means for Solving the Problem] This invention is the activity approach of the trash of form polystyrene, grinding or after reducing the volume or pelletizing, it dissolves the collected form polystyrene in a halogenated hydrocarbon system solvent, it removes insoluble matter, subsequently comes out, brominates this solution, and relates to the approach of manufacturing bromination polystyrene.

[0005] It is desirable to be able to use foam, such as polystyrene, a styrene maleic anhydride copolymer, a polyethylene-styrene graft copolymer, a styrene-butane diene copolymer, an acrylonitrile styrene copolymer, and acrylonitrile-butadiene-styrene copolymer, and to contain a styrene component 80% of the weight or more at least as form polystyrene used by this invention.

[0006] Form polystyrene may be mold goods and a foaming board, rose-like shock absorbing material, etc. which are used as building materials, such as foaming sheets, such as tableware containers, such as bead foaming articles, such as a home wrapping material and a fish box for fishery, a food-grade tray, and instant noodles, and a heat insulator, are used. Moreover, the foaming product colored or printed can also be used. Furthermore, the cut article with which the particle size of a foaming bead separated from specification, or the recovery article of the weld flash at the time of shaping can also be used.

[0007] When the collected form polystyrene is packaging and the foaming article by which fabricating was carried out, foreign matters, such as a label, a union string, and rubber material, are contained in many cases. Moreover, foreign matters are resin material, such as components other than form polystyrene, polypropylene, polyethylene terephthalate, and vinyl chloride resin, and the foam of those, and a metal body still like aluminum in many cases. Then, the activity which carries out separation sorting of the foreign matter in advance of regeneration of recovery form polystyrene is required.

[0008] the recovery form polystyrene used by this invention -- grinding -- or it is necessary to reduce the volume or pelletize, and can be used as a raw material of the bromination polystyrene of this invention. since it is hard to treat ** greatly when manufacture on transportation, storage, and industrialization level is considered although it is possible to use recovery form polystyrene as a raw material of bromination polystyrene as it is, without carrying out processing of grinding, reduction, or pelletizing -- grinding -- or it is necessary to reduce the volume or pelletize and to enlarge

specific gravity Coarse grinding of the form polystyrene after carrying out separation sorting of the foreign matter is carried out, it is pulverized further, and a grinding article is obtained. Or with the extruder after coarse grinding, after melting and extrusion, it can judge and can return to the resin of a pellet type. Moreover, after filtering a foreign matter at the wire gauze which fused with the extruder, without doing a separation sorting activity while the foreign matter had been intermingled, and was formed near the outlet of an extruder into recovery form polystyrene when the above foreign matters were not intermingled so much, it can extrude from nozzle metal mold etc., and can also judge and pelletize. Moreover, while pulverizing-izing by carrying out coarse grinding mechanically [when a foreign matter is contained below for a constant rate in recovery form polystyrene] as it is, and applying shearing force again mechanically in this coarse-grinding object, carry out a temperature up with frictional heat more than the softening temperature of polystyrene, and it is made to soften, and most air bubbles are deaerated, and the volume is made to reduce. Furthermore, an impact type pulverizer can grind this deaerated pulverizing object to an indeterminate form resin particle below with the softening temperature of polystyrene. for example, in the recovery form polystyrene by which 10 or less % of the weight of the foreign matter was intermingled While carrying out coarse grinding mechanically and applying and pulverizing-izing shearing force again mechanically in this coarse-grinding object Carry out a temperature up with frictional heat more than the softening temperature of polystyrene, make it soften, deaerate and reduce most air bubbles, and the volume of foam is made into or less about 1 / 5. Furthermore, what ground the deaerated this pulverizing object to the indeterminate form resin particle with the impact type pulverizer below with the softening temperature of polystyrene can be used suitably.

[0009] As mentioned above, grinding or the polystyrene reduced or pelletized can also be brominated as it is, after dissolving in a halogenated hydrocarbon solvent, but in order to obtain the bromination polystyrene which was excellent in thermal resistance as a flame retarder, it is necessary to remove said solvent insoluble matter by approaches, such as filtration and centrifugation. Furthermore, after the dissolution, after adding adsorbents, such as diatomaceous earth, silica gel, activated clay, and activated carbon, and making insoluble matter adsorb, it is more desirable to carry out filtration removal. As a halogenated hydrocarbon solvent, bromination hydrocarbons, such as chlorinated hydrocarbons, such as a methylene chloride, chloroform, a carbon tetrachloride, ethylene dichloride, 1,1,1-trichloroethane, a trichloroethylene, tetrachloroethylene, and mono-chlorobenzene, a methylene bromide, and ethylene dibromide, are used. When bromination is presented without removing insoluble matter The fusion inhibitor at the time of the pre-expansion of the manufacture included in the collected form polystyrene, Finishing agents, such as a welding accelerator at the time of shaping, and an antistatic agent, cellular adjustment, and a cellular stabilizer, When the unstable compound generated thermally, and the bromination polystyrene obtained becomes a thing inferior to thermal resistance and it blends with resin as a flame retarder with additives, such as lubricant and a foaming agent, decomposition and a coloring phenomenon are caused and the commodity value of mold goods is reduced.

[0010] Next, the polystyrene which dissolved in said solvent is brominated by the general approach. For example, a bromine, a bromine chloride, etc. can be used as a brominating agent. As a catalyst of bromination, metals, such as Lewis acid, such as anhydrous salt-sized aluminum, the anhydrous salt-sized second iron, and an antimony trichloride, or aluminum, iron, and antimony, can be used. -20-100 degrees C of reaction temperature are desirable. After the bromination polystyrene solution after a bromination reaction carries out rinsing neutralization and removes acid content and mineral salt, it can obtain the bromination polystyrene of fine particles or a solid-state by dropping a solvent into poor solvents, such as distilling off or a methanol, and ethanol.

[0011] The bromine content of the bromination polystyrene obtained by the approach of this invention is desirable when that it is 20 - 70 % of the weight takes into consideration the use as a flame retarder of inflammable resin.

[0012] As inflammable resin, polystyrene, styrene resin like ABS, polyolefine like polyethylene or polypropylene, thermoplastic polyester like polyethylene terephthalate or polybutylene terephthalate, Nylon 66, a polyamide like Nylon 46, etc. are mentioned.

[0013]

[Example] This invention is not limited by these examples, although an example is given to below and this invention is further explained to a detail.

[0014] Synthetic (example 1) 1L of bromination polystyrene Within a glass reactor (it has churning equipment, a capacitor, a thermometer, a dropping funnel, and a gas absorber), it is 75g of recovery reduction articles of form polystyrene. Ethylene dichloride (Following EDC is called) 750g It dissolves and is 20g of diatomaceous earth further. After making insoluble matter adsorb in addition, agitating, nutsche filtration removed insoluble matter and diatomaceous earth. It is 6g of antimony trichlorides to filtrate. 370g of EDC solutions of 70% of the weight of the bromine chloride beforehand adjusted while keeping the internal temperature at 15-25 degrees C, agitating, after carrying out the churning dissolution in addition It was dropped over 2 hours and made to ripe at further 15-25 degrees

C for 1 hour. After returning a superfluous bromine chloride after aging termination and neutralizing and rinsing the EDC solution of bromination polystyrene, it was dropped into the methanol and crystallization was carried out. Bromination polystyrene 205g of after filtration desiccation and fine particles It obtained. The bromine content of the obtained bromination polystyrene was 68.5%. The result of having analyzed a bromine content, thermogravimetric analysis (5%, 10% weight reduction temperature), the appearance hue, and the amount of heating generating HBr(s) is shown in Table 1. Moreover, analysis was performed by the following approaches.

[0015] - The bromine content was measured by the approach according to a flask combustion method (JIS K-7299).

- The thermostat flex time 8100 (Rigaku make) was used for thermogravimetric analysis as a measuring device.

Moreover, an ambient atmosphere is air (about 50 ml/min), and a programming rate is 10degree C/min. It measured by carrying out.

- The appearance hue was measured with the color color difference meter (the Minolta Camera make, CR-100 mold), and was searched for as a value of L, a, and b display system.

- the gas absorption bottle (100ml of distilled water) which the amount of heating generating HBr(s) set the heating tube to the electric furnace, blew in further, and was equipped with tubing -- connecting -- an electric furnace -- nitrogen gas (about 50 ml/min) -- through and 3g of samples the amount of bromines of gas absorption water after putting into a heating tube and heating at 200 degrees C for 1 hour -- Bolu Hurd -- quantitative analysis was carried out by law.

[0016] (Example 2) It sets in the example 1 and is EDC750g of a solvent. 1,500g of methylene bromides It is 370g of EDC solutions of the bromine chloride of a brominating agent to anhydrous salt-sized aluminum about the antimony trioxide of a catalyst. 359g of bromines It is 208g of fine particles of bromination polystyrene with the same approach as an example 1 except having changed. It obtained. An analysis result is shown in Table 1.

[0017] (Example 1 of a comparison) It is 213g of fine particles of bromination polystyrene with the same approach as an example 1 except having presented bromination as it is in the example 1, without performing adsorption and filtration of insoluble matter from the EDC solution of the polystyrene before bromination. It obtained. An analysis result is shown in Table 1.

[0018]

[Table 1]

表 1

	実施例 1	実施例 2	比較例 1
臭素化剤	塩化臭素	臭素	塩化臭素
触媒	SbCl ₃	AlCl ₃	SbCl ₃
臭素化前の不溶物の濾過	有	有	無
臭素含有量 (%)	68.5	67.9	61.5
T G A 5%重量減少温度 (°C)	357	353	342
50%重量減少温度 (°C)	401	399	373
加熱発生HBr量 (%)	0.04	0.12	0.50
外観色相 (L値)	94.8	92.3	85.2

[0019] To the evaluation (examples 3 and 4 and example 2 of comparison) polyethylene terephthalate (Teijin TR-4550BH) of the fire retardancy and the mechanical characteristic of resin mold goods The bromination polystyrene, the antimony trioxide (NIHON SEIKO ATOX-S) which were obtained in examples 1 and 2 and the example 1 of a comparison, By the blending ratio of coal which shows a glass fiber (3MA429made from Asahi fiberglass-A) in Table 2, after mixing, It kneaded with the laying temperature of 280 degrees C with the twin screw extruder (RY-30made from ****-30-VS3.7), and immediately after extruding from the nozzle metal mold attached at the tip of an extruder, the extruded strand was cooled underwater and it pelletized by the pelletizer. After drying this pellet at 120 degrees C for 24 hours, using the injection molding machine (product F85 made from KUROKUNA), it fabricated with the cylinder temperature of 240-265 degrees C, and the die temperature of 140-150 degrees C, and the test piece was obtained. The physical-properties trial was performed by the following approach about the obtained test piece. The test result is shown in Table 2.

- Heat deflection temperature is JIS. K It measured by the approach according to 7207.

- Flexural strength is JIS. K It measured by the approach according to 7203.
- Tensile strength is JIS. K It measured by the approach according to 7113.
- The combustion test was measured by the approach according to UL94 (1/16 inch).
- An oxygen index is JIS. K It measured by the approach according to 7201.

[0020]

[Table 2]

表2
配合割合（単位：重量部）

		実施例3	実施例4	比較例2
配 合 割 合	P E T樹脂	100	100	100
	臭素化ポリスチレン	実施例1 で得たもの	実施例2 で得たもの	比較例1 で得たもの
		15	15	15
	三酸化アンチモン	5	5	5
物 性 試 験 結 果	ガラス繊維	50	50	50
	熱変形温度 (°C)	236.5	235.5	221.5
性 試 験 結 果	曲げ強度 (kg/mm²)	19.1	19.6	15.3
	曲げ弾性率(kg/mm²)	1,074	1,171	957
性 試 験 結 果	引張強度 (kg/mm²)	14.1	11.8	8.5
	破断伸び (%)	1.6	1.2	0.5
性 試 験 結 果	燃焼試験 (1/16 インチ)	V-0	V-0	V-2
	酸素指数	34.2	33.8	30.2

[0021] (Examples 5 and 6 and example 3 of a comparison) To Nylon 66 resin (Toray Industries ARAMIN CM3001N) The bromination polystyrene, the antimony trioxide (NIHON SEIKO ATOX-S) which were obtained in examples 1 and 2 and the example 1 of a comparison, By the blending ratio of coal which shows a glass fiber (03MAFT(s)[made from the Asahi fiberglass]-2A) in Table 3, after mixing, It kneaded with the laying temperature of 240-260 degrees C with the twin screw extruder, and immediately after extruding from the nozzle metal mold attached at the tip of an extruder, the extruded strand was cooled underwater and it pelletized by the pelletizer. After carrying out the vacuum drying of the obtained pellet at 80 degrees C for 5 hours, using the injection molding machine, it fabricated with the cylinder temperature of 255-265 degrees C, and the die temperature of 100 degrees C, and the test piece was obtained. About the obtained test piece, the physical-properties trial was performed with the same test method as examples 3 and 4 and the example 2 of a comparison. The result is shown in Table 3.

[0022]

[Table 3]

表3

配合割合 (単位:重量部)

		実施例5	実施例6	比較例3
配合割合	ナイロン66	100	100	100
	臭素化ポリスチレン	実施例1 で得たもの	実施例2 で得たもの	比較例1 で得たもの
		30	30	30
	三酸化アンチモン	8	8	8
	ガラス繊維	60	60	60
物性試験結果	熱変形温度 (°C)	242.5	241.7	240.4
	曲げ強度 (kg/mm ²)	20.6	21.2	15.3
	曲げ弾性率(kg/mm ²)	928	899	543
	燃焼試験 (1/16 インチ)	V-0	V-0	V-2
	酸素指数	34.3	33.7	30.8

[0023]

[Effect of the Invention] The bromination polystyrene which is obtained according to this invention uses the collected form polystyrene as a raw material, and contributes to society as the effective activity approach of these trash. Moreover, the obtained bromine polystyrene should be excellent in an appearance hue and thermal resistance, and especially the mold goods obtained from the resin constituent which blended bromination polystyrene with inflammable resin should be excellent in fire retardancy, thermal resistance, and a mechanical characteristic. That is, since it is removed before the various additives contained in the collected form polystyrene brominating and an unstable compound does not generate thermally by bromination, also when it is used as a flame retarder, it can excel, mold goods can be obtained and commodity value can be raised.

[Translation done.]